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This report describes the progress made under the present contract. It is presented in three main sections dealing, respectively, with structure-property relations, with blends, and with block copolymers. In the area of structure-property relations, one paper is particularly noteworthy in that it presents a new model for the morphology of ionomers which is consistent with all known experimental results, including small angle X-ray scattering and mechanical properties, among many others. In the blend area, the most notable result pertains to the achievement of controlled miscibility between nylon and polystyrene. Finally, in the block copolymer area, a completely new two dimensional micelle morphology was discovered at air-water interfaces. These studies represent the highlights of the broad investigation of the effect of coulombic interactions on the properties of polymer in the bulk, in solution, and on surfaces.

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Final Report

Submitted by Dr. A. Eisenberg

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I. Introduction

This report describes the progress made under the present contract during the period Oct 1 1987 to May 31 1991. It will be presented in three main sections dealing, respectively, with structure-property relations, with blends, and with block copolymers. In the area of structure-property relations, one paper is particularly noteworthy in that it presents a new model for the morphology of ionomers which is consistent with all known experimental results, including small angle X-ray scattering and mechanical properties, among many others. In the blend area, the most notable result pertains to the achievement of controlled miscibility between nylon and polystyrene. Finally, in the block copolymer area, a completely new two dimensional micelle morphology was discovered at air-water interfaces. These studies represent the highlights of the broad investigation of the effect of coulombic interactions on the properties of polymer in the bulk, in solution, and on surfaces.

II. Structure-Property Relations

In the first study of this topic, the high-temperature dispersions occurring in some poly(styrene-co-alkali methacrylate) ionomers were investigated by dynamic

mechanical thermal analysis as a function of ion content. The heights and areas of the loss modulus peaks associated with these dispersions suggest that the ionic "cluster" phase becomes the dominant and perhaps even continuous phase above an ion concentration of ca. 6 mol %. Apparent activation energies of these high-temperature transitions support the phase-separated cluster model and indicate that the dispersions are true glass transitions (publ. # 8).

Another aspect concerned the investigation of ionomers in which the ions were located ends of pendant side chains. The dynamic mechanical properties of two analogous series of alkylated styrene ionomers were examined. The samples were prepared in the partial base hydrolysis of precursors containing 10-15 mol % of 4-substituted styrene units with substituents $R = -(\text{CH}_2)_n\text{CO}_2\text{Me}$ ($n = 1, 5, 10$) or $R = -\text{O}(\text{CH}_2)_n\text{CO}_2\text{Me}$ ($n = 1, 4, 10$). The variation in the mechanical properties was studied as a function of ion content for the different ionomers, to yield a systematic investigation of the effects of ion spacing from the polymer backbone. Three distinct factors are postulated as having contributed to the trends observed among the different series of compounds. These include the bulkiness and rigidity of the units to which the ionic groups are attached

and the immobilizing effect of the ionic groups on the polymer backbone. Furthermore, in the ether derivatives, the presence of alkyl aryl ether linkages leads to solvation effects and thus reduces clustering (publ. # 6).

This investigation was supplemented by a study in which small-angle X-ray scattering was used to investigate the morphology of these random, styrene-based ionomers that have ionic groups placed at the ends of variable-length side chains. The SAXS peaks were interpreted as arising from interparticle interferences, and the changes in peak position with increasing side-chain length were attributed to increasing distances between the scattering centers. The decrease in the width of the SAXS peaks with increasing side-chain length was attributed to an increased organization of the ionic domains for the long side-chain ionomers. The Bragg spacing was found to increase linearly both with increasing side-chain length and with increasing average separation distance between the ionic groups. Furthermore, the radii of the ionic aggregates were found to be independent of the ionic content and limited in size by the proximity of the bulky polystyrene backbone. Since previous SAXS data from copolymers of polystyrene with cesium methacrylate are in excellent agreement with the

morphological trends observed in this study, it is suggested that a morphological continuity exists for styrene ionomers that have their ionic groups placed very close to the backbone of ionomers with large separations between their ionic groups. By extension, the morphological continuity is suggested to include also the halato telechelics (publ. # 11).

All these studies led to the reexamination of the morphology of these materials, as a result of which a new morphological model for random ionomers was proposed which incorporates the findings of the recent dynamic mechanical and X-ray scattering studies. The model is based on the existence of multiplets, which reduce the mobility of the polymer chains in their vicinity. The thickness of the restricted mobility layer surrounding each multiplet is postulated to be of the order of the persistence length of the polymer. Isolated multiplets act as large cross-links, thus increasing the glass transition temperature of the material. As the ion content is increased, the regions of restricted mobility surrounding each multiplet overlap to form larger contiguous regions of restricted mobility. When these regions become sufficiently large, they exhibit phase-separated behavior and are termed clusters. The model is in

good agreement with a very wide range of experimentally observed phenomena, especially those based on dynamic mechanical and X-ray scattering techniques. This represents a completely new view of ionomers in that it reconciles dynamic mechanical and morphological studies in a unique and unambiguous way (publ. # 7).

III. Block Ionomers

The studies on block ionomers are reported separately because they represent a very extensive series of investigations spanning the bulk state, non-aqueous solutions, and air-water interfaces. In one of the bulk studies, block copolymers consisting of long styrene midblocks and much shorter 4-vinyl pyridine end-blocks were quaternized with n-iodo alkanes ($2 \leq n \leq 10$) to give block ionomers of a novel architecture. The name "bottlebrush" seems appropriate for these materials. A preliminary investigation of the morphology of these systems, prepared by in situ quaternization, was the subject of the first study. The morphology is dependent on both the length of the iodo alkane and the relative sizes of the blocks. Even with identical sample histories, two distinct morphologies are seen. One of these is characterized by a single broad SAXS peak, while the other shows a much narrower peak and

higher-order features. The latter morphology is associated with the higher ionic to nonionic ratios and long side chains (publ. # 10).

In another, as yet unpublished, investigation, a detailed study was performed of the bulk properties of methyl quaternized materials of the AB diblock structure. Spherical ionic inclusions were identified, the radius of which is similar to the fully stretched length of the ionic chain. The same relationship is seen for cesium methacrylate blocks. By contrast, a neutron scattering study of the polystyrene dimensions revealed that these were the same as the unperturbed dimensions of PS. This behavior can be understood qualitatively simply on the basis of surface energy arguments.

When these AB diblock copolymers are dissolved in non-aqueous solvents (good for PS) aggregates are formed which consist of ionic cores surrounded by a polystyrene corona. Two studies were devoted to these materials.

Monolayers of a polystyrene/poly-4-vinylpyridine AB diblock ionomer, $(PS)_{260} (PVP)_{240}$, fully quaternized with decyl iodide have been studied at the air/water interface using the Langmuir film balance technique. Surface pressure/area isotherms exhibit abrupt onset pressures and

an apparent first order phase transition at high pressures. Transmission electron micrographs of LB films deposited on carbon-coated copper grids provide direct evidence of self-assembly of the diblock copolymers into circular surface micelles. These surface micelles are highly regular, have an aggregation number of ~ 110 , and appear to have almost (at low surface pressures) fully extended dec-PVP⁺ chains extending radially from a central core of PS coils. These aggregates pack with a surface density $\sim 10^{10}$ particles per cm² at the lowest detectable surface pressures. The apparent first-order phase transition correlates with electron micrograph observations, where the decylated polyelectrolyte block proceeds from a surface-adsorbed state to a submerged, aqueous state as the film is compressed. The entropy of this transition (descriptively called a "starfish-jellyfish" transition) is +6.3 e.u. and is consistent with the polymeric micelles passing from an ordered 2D state to a less ordered quasi-2D state (publ. # 16).

Extensive studies were also devoted to electron microscopy of AB diblocks at air-water interfaces, using both classical EM and atomic force microscopy (publ. # 14).

In a subsequent publication, five independent methods for calculating the aggregation number N of the block ionomer surface micelles were presented. Each method relies on the examination of transmission electron photomicrographs of LB films. The values of N fall in the range of 83 to 146 with greatest confidence placed on the individual micelle area method ($N = 131 \pm 35$). Good agreement between all the calculation methods suggests that the model presented (see above) to describe the unusual entropically driven phase transition observed in π -A isotherms for polystyrene-block decylated polyvinylpyridinium iodide is a reasonable one (publ. # 15).

Very detailed studies of the morphology and of the transition behavior have been performed, and will be the subject of several (probably four) additional publications.

IV. Blends

A range of studies has been performed on blends. The subject of ion-pair - ion-pair interaction as well as ion-ion interaction in the absence of protons was of special interest in the early stages. Miscibility enhancement of ionomer-ionomer and ionomer-polymeric acid system was studied on the polymer pairs of poly(styrene-co-tetramethyl ammonium styrenesulfonate)/poly(ethyl acrylate-co-N-methyl-

4-vinylpyridinium iodide) and poly(styrene-co-styrenesulfonic acid)/poly(ethyl acrylate-co-N-methyl-4-vinylpyridinium iodide). NMR and dynamic mechanical results show that in these blends direct macroion-macroion interaction can be achieved with the elimination of microcounterions from the polymer chains. Ion-ion attraction leads to a miscibility enhancement comparable to that of the previously reported proton transfer blends; a miscible blend is obtained with ca. 5 mol% of ions in the polymers (publ. # 5).

A subsequent study was devoted to direct ion-ion interactions. Direct ion-ion interactions in ionomer blends are achieved through microion elimination by mixing the two ionomers, poly(styrene-co-tetraalkylammonium methacrylate) and poly(ethyl acrylate-co-N-methyl-4-vinyl pyridinium iodide), in a benzene/methanol mixture. The pyridiniumcarboxylate ion-ion interaction are compared with pyridinium-sulfonate interactions which were described before. It is shown that carboxylate ions are much less effective than sulfonate ions in enhancing miscibility in the polystyrene/poly(ethyl acrylate) system. Complete miscibility is not attained for this polymer pair even with up to 10 mol % ions. In another system, ion pair-ion pair

blends were prepared by mixing poly(styrene-co-sodium styrenesulfonate) with poly(ethyl acrylate-co-N-methyl-4-vinyl pyridinium iodide), also in a benzene/methanol mixture. The results show that ion pair-ion pair associations are also much weaker driving force for miscibility enhancement in this polymer pair than the corresponding direct pyridinium-sulfonate ion-ion interactions. A ranking is presented of the relative strengths of the various ionic interactions in their effect on miscibility enhancement, which also includes ion-dipole interactions (sodium sulfonate-pyridine) (publ. # 9).

Polyurethane blends remained on the agenda. Blending of a poly(ether urethane) with a polyphosphonate obtained by phase transfer catalyzed polycondensation of 4,4'-biphenol and chloromethylphosphonic dichloride generates a phase-separated material. One phase contained the soft segment of the polyurethane. This has been excluded from a high- T_g phase that contains ionic species formed mainly by proton transfer and elimination reactions between the hard segment of the polyurethane and the polyphosphonate. Two glass transitions appear in the blend: one close to the T_g of the polyphosphonate and one belonging to the excluded soft segment of the polyurethane. The low temperature T_g

decreases with increasing polyphosphonate content, while the high temperature transition increases slightly, indicating an increase in the purity of the soft segment and the presence of ionic interactions in the hard segment. The presence of ionic interactions is confirmed by NMR analysis of the blend. Comparison of the spectra of the blends with those of the pure components, along with two-dimensional experiments, indicate a reaction involving the chloromethyl groups of the polyphosphonate and the nitrogens of the polyurethane (publ. # 1).

Two systems of special interest were based on blends of poly(tetrafluoro ethylene) and blends of nylon. In one paper, it was shown that ion-ion interactions resulting from a proton transfer induce considerable miscibility in blends of functionalized poly(tetrafluoroethylene) with ethyl acrylate copolymers containing 4-vinyl pyridine. Dynamic mechanical measurements, in conjunction with transparency of the samples, are used to evaluate miscibility. It is shown that mixing conditions exert a strong effect on the properties of the final blend. The glass transition of the blend is shown to be strong function of the blend composition, as is characteristic of highly miscible systems (publ. # 3).

A very recent study was devoted to blends of Nylon 6. Nylon 6 and polystyrene are compatibilized when the polystyrene is functionalized with as little as 2.2 mol % sulphonic acid groups. Evidence of this is provided by scanning electron microscopy and dynamic mechanical studies. However, some hydrolysis of the nylon 6 appears to take place at processing temperatures (240-250°C). No hydrolysis of the nylon 6 is evident when the sulphonic acid groups are neutralized with lithium or sodium. The lithium-neutralized material causes significant miscibility enhancement as seen from the melting point depression in the blend, suggesting a strong interaction. Sodium salts are ineffective. Several additional studies in this area are in progress (publ. # 18). A range of additional studies are underway and will be published in the future. Partial ARO sponsorship will naturally be acknowledged.

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19. R.B. Moore, A. Molnar, C.E. Williams and E. Eisenberg, "Ionic Aggregation in Sulfonated and Hydrogenated Poly(Styrene-co-Butadiene) Ionomers".
20. R.B. Moore, M. Gauthier, C.E. Williams and A. Eisenberg, "Heterogenieties in Random Ionomers. A Small X-Ray Scattering Investigation of Alkylated Polystyrene Based Materials".
21. A. Desjardins and A. Eisenberg, Colloidal Properties of Block Ionomers II.

Macromolecules

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